

Claims

1. A method for producing a group IB-IIIA-VIA quaternary or higher alloy semiconductor film, the method comprising the steps of:
- 5 (i) providing a metal film comprising a mixture of group IB and group IIIA metals;
- 10 (ii) heat treating the metal film in the presence of a source of a first group VIA element (said first group VIA element being hereinafter referred to as VIA₁) under conditions to form a first film comprising a mixture of at least one binary alloy selected from the group consisting of a group IB-VIA₁ alloy and a group IIIA-VIA₁ alloy; and at least one group IB-IIIA-VIA₁ ternary alloy,
- 15 (iii) optionally heat treating the first film in the presence of a source of a second group VIA₂ element (said second group VIA element being hereinafter referred to as VIA₂) under conditions to convert the first film of step (ii) into a second film comprising at least one alloy selected from the group consisting of a group IB-VIA₁-VIA₂ alloy and a group IIIA-VIA₁-VIA₂ alloy; and the at least one group IB-IIIA-VIA₁ ternary alloy of step (ii); and
- 20 (iv) heat treating either the first film of step (ii) or second film of step ((iii)) to form a group IB-IIIA-VIA quaternary or higher alloy semiconductor film.
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2. The method according to claim 1, wherein the mixture of the first film of step (ii) is a stable mixture such that the molar ratio of all the group IB-VIA₁ and/or group IIIA-VIA₁ alloys to all the at least one group IB-IIIA-VIA₁ ternary alloy remains substantially constant.
3. The method according to claim 1, wherein the metal film of step (i) is provided on a substrate optionally coated with a metal layer.
4. The method according to claim 3, wherein the metal layer is a Mo layer.
5. The method according to claim 1, wherein the metal film of step (i) comprises a mixture of metals selected from the group consisting of Cu, In and Ga.
6. The method according to claim 5, wherein the metal film of step (i) is a Cu-In-Ga alloy metal film.
7. The method according to claim 5, wherein the metal film is a Cu-In alloy metal film.
8. The method according to claim 1, wherein the group VIA₁ element is Se.
9. The method according to claim 1, wherein a source of the group VIA₁ element is a gaseous mixture of H₂Se and at least one inert gas.
10. The method according to claim 9, wherein the inert gas is Ar.

11. The method according to claim 9, wherein the molar concentration of Se relative to the at least one inert gas is from 0.01 to 15 molar percent.
- 5 12. The method according to claim 11, wherein the molar concentration of Se relative to the at least one inert gas is from 0.05 to 0.3 molar percent.
- 10 13. The method according to claim 1, wherein step (ii) is carried out at a reaction temperature from 300 to 500°C.
14. The method according to claim 13, wherein step (ii) is carried out at a reaction temperature from 350 to 450°C.
- 15 15. The method according to claim 13, wherein the metal film of step (i) is heated rapidly to a reaction temperature of between 300 to 500°C within 5 minutes.
- 20 16. The method according to claim 1, wherein during step (ii) the metal film of step (i) is exposed to the source of VIA₁ for a period from 10 to 120 minutes.
- 25 17. The method according to claim 16, wherein the metal film of step (i) is exposed to the source of VIA₁ for a period from 30 to 60 minutes.
- 30 18. The method according to claim 1, wherein the first film of step (ii) has below 50 atomic % of the VIA₁ element.
19. The method according to claim 8, wherein the first film of step (ii) has below 50 atomic % of Se.

20. The method according to claim 1, wherein the first film of step (ii) is treated under conditions to ensure that the mixture of the at least one binary alloy and the at least one group IB-
5 IIIA-VIA₁ ternary alloy remains stable.
21. The method according to claim 20, wherein the source of the V1A₁ element is removed so as to maintain the stability of the mixture.
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22. The method according to claim 20, wherein the first film of step (ii) is exposed to an inert atmosphere for 5 to 20 minutes.
- 15 23. The method according to claim 20, wherein the first film of step (ii) is cooled to temperatures below 200°C.
24. The method according to claim 5, wherein the first film of step (ii) comprises a mixture of at least one binary alloy selected
20 from the group consisting of InSe, CuSe and Ga₂Se₃ and at least one ternary alloy selected from the group consisting of CuInSe₂ and CuGaSe₂, where VIA₁ is Se.
25. The method according to claim 1 which is for producing a group IB-IIIA-VIA pentenary alloy semiconductor film, and
25 wherein:
- step (i) comprises providing a metal film including a mixture of at least one group IB element, a first group
30 IIIA element (the first group IIIA element hereinafter being referred to as IIIA₁) and a second group IIIA element (the second group IIIA element hereinafter being referred to as IIIA₂);

- 5 - step (ii) comprises heat treating the metal film of step (i) in the presence of a source of VIA_1 under conditions to form a first film comprising a mixture of binary alloys selected from the group consisting of a group IB- VIA_1 alloy, a group IIIA₁- VIA_1 alloy and a group IIIA₂- VIA_1 alloy and two ternary alloys, namely a group IB-IIIA₁- VIA_1 alloy and a group IB-IIIA₂- VIA_1 alloy;
 - 10 - step (iii) is carried out and comprises heat treating the first film of step (ii) in the presence of a source of VIA_2 under conditions to convert the first film of step (ii) into a second film comprising at least one alloy selected from the group consisting of a group IB- VIA_1 - VIA_2 alloy, a group IIIA₁- VIA_1 - VIA_2 and a group IIIA₂- VIA_1 - VIA_2 alloy;
 - 15 and the ternary alloys of step (ii); and
 - 20 - step (iv) comprises heat treating the second film of step (iii) to form a group IB-IIIA₁-IIIA₂- VIA_1 - VIA_2 pentenary alloy semiconductor film.
26. The method of claim 25, wherein the first film of step (ii) includes a mixture of binary alloys in the form of a group IB- VIA_1 alloy, a group IIIA₁- VIA_1 alloy and a group IIIA₂- VIA_1 alloy and ternary alloys in the form of a group IB-IIIA₁- VIA_1 alloy and a group IB-IIIA₂- VIA_1 alloy and wherein the second film of step (iii) includes a mixture of alloys in the form of a group IB- VIA_1 - VIA_2 alloy, a group IIIA₁- VIA_1 - VIA_2 and a group IIIA₂- VIA_1 - VIA_2 alloy and the ternary alloys of step (ii).
27. The method according to claim 26, wherein step (iv) comprises a first heat treatment step wherein the second film of step (iii) is heated to form a third film comprising a mixture of quaternary alloys selected from the group consisting of a group IB-IIIA₁- VIA_1 - VIA_2 alloy and a group IB-IIIA₂- VIA_1 - VIA_2

alloy; and then subjecting the third film to a second heat treatment step wherein the third film is annealed so as to form a group IB-IIIA₁-IIIA₂-VIA₁-VIA₂ pentenary alloy semiconductor film.

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28. The method according to claim 27, wherein the first heat treatment step of step (iv) comprises heating the second film of step (iii) in the presence of a source of VIA₂ so as to form the third film.

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29. The method according to claim 28, wherein the second film of step (iii) is exposed to the source of VIA₂ for a period of from 5 to 10 minutes.

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30. The method according to claim 29, wherein the first heat treatment step of step (iv) comprises heating the second film of step (iii) at a temperature from 450 to 600°C so as to form the third film.

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31. The method according to claim 30, wherein the first heat treatment step of step (iv) comprises heating the second film of step (iii) at a temperature from 500 to 550°C.

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32. The method according to claim 27, wherein the second heat treatment step of step (iv) comprises annealing the third film for 15 to 90 minutes.

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33. The method according to claim 32, wherein the second heat treatment step of step (iv) comprises annealing the third film at a temperature from 500°C to 600°C.

34. The method according to claim 33, wherein the second heat treatment step of step (iv) comprises annealing the third film at a temperature from 520°C to 580°C.
- 5 35. The method according to either one of claims 26 and 27, wherein IB is Cu, IIIA₁ is In, IIIA₂ is Ga, VIA₁ is Se and VIA₂ is S.
- 10 36. The method according to claim 35, wherein the second heat treatment step of step (iv) comprises annealing the third film under conditions so as to form a pentenary alloy having the general formula II:
- $$\text{Cu}(\text{In}_{1-x}\text{Ga}_x)(\text{Se}_{1-y}\text{S}_y)_2 \dots\dots\dots (\text{I})$$
- 15 37. The method according to claim 35, wherein a source of S is a gaseous mixture of H₂S and at least one inert gas.
- 20 38. The method according to claim 37, wherein the molar concentration of S relative to the at least one inert gas is from 0.1 to 10 molar percent.
- 25 39. The method according to claim 38, wherein the molar concentration of S relative to the at least one inert gas is from 0.3 to 0.5 molar percent.
- 30 40. The method according to claim 25, wherein, in step (iii), the first film of step (ii) is heat-treated at a temperature of from 100 to 500°C.
41. The method according to claim 40, wherein, in step (iii), the first film of step (ii) is heat-treated at a temperature of 450°C.

42. The method according to claim 40, wherein, in step (iii), the first film of step (ii) is heat-treated for a period of from 5 to 10 minutes.
- 5 43. The method according to claim 25 which is for producing a group IB-IIIA-VIA alloy semiconductor film, and wherein
- 10 - step (i) comprises providing a metal film comprising a mixture of Cu, In and Ga;
 - 15 - step (ii) comprises heat treating the metal film in the presence of a gaseous mixture of H_2Se and at least one inert gas, wherein the molar concentration of Se relative to the at least one inert gas is from 0.05 to 0.3%, at a temperature of from 350°C to 450°C , for a period of between 30 to 60 minutes, so as to form a first film comprising a mixture of binary alloys in the form of CuSe , InSe , Ga_2Se_3 and the ternary alloys, namely CuInSe_2 and CuGaSe_2 ;
 - 20 - step (iii) comprises heat treating the first film of step (ii) in the presence of a gaseous mixture of H_2S and at least one inert gas, at a temperature from 400°C to 500°C , for a period from 5 to 10 minutes, so as to form a second film comprising a mixture of sulfoselenides in the form of $\text{Cu}(\text{Se},\text{S})$, $\text{In}(\text{Se},\text{S})$ and $\text{Ga}(\text{Se},\text{S})$ and the ternary alloys of step (ii); and
 - 25 - step (iv) comprises heat treating the second film of step (ii) in the presence of H_2S in Ar, at a temperature of from 500°C to 550°C , for 5 to 10 minutes such that the sulfoselenides react with the ternary alloys of step (ii) to form a third film comprising a mixture of $\text{CuIn}(\text{Se},\text{S})_2$ and
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CuGa(Se,S)₂, and subsequently annealing the mixture of CuIn(Se,S)₂ and CuGa(Se,S)₂ at a temperature of from 520°C to 580°C so as to form a pentenary alloy having the general formula (I).

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44. The method according to claim 1 which is for producing a group IB-IIIA-VIA quaternary alloy semiconductor film, and wherein:

10 - step (i) comprises providing a metal film including a mixture of at least one group IB element, a first group IIIA element (the first group IIIA element hereinafter being referred to as IIIA₁) and a second group IIIA element (the second group IIIA element hereinafter being referred to as IIIA₂);

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 - step (ii) comprises heat treating the metal film of step (i) in the presence of a source of VIA₁ under conditions to form a first film comprising a mixture of binary alloys selected from the group consisting of a group IB-VIA₁ alloy, a group IIIA₁-VIA₁ alloy and a group IIIA₂-VIA₁ alloy and a ternary alloy being a group IB-IIIA₁-VIA₁ alloy;

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25 - step (iv) comprises heat treating the first film of step (ii) to form a group IB-IIIA₁-IIIA₂-VIA₁ quaternary alloy semiconductor film.

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45. The method according to claim 44, wherein the heat treatment of step (ii) is carried out at a reaction temperature of 400°C.

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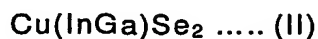
46. The method according to claim 44, wherein step (iv) comprises a first heat treatment step wherein the first film of step (ii) is heated and then subsequently a second heat

treatment step wherein the first film is annealed so as to form a group IB-III_A₁-III_A₂-VI_A₁ quaternary alloy semiconductor film.

- 5 47. The method according to claim 46, wherein the first heat treatment step of step (iv) comprises heating the first film of step (ii) to a reaction temperature of from 100 to 600°C.
- 10 48. The method according to claim 46, wherein the second heat treatment step of step (iv) comprises first annealing the first film of step (ii) in the presence of an inert gas and then subsequently annealing the first film in the presence of a source of VI_A₁.
- 15 49. The method according to claim 48, wherein the first film of step (ii) is first annealed in the presence of the inert gas at a temperature of from 100 to 600°C.
- 20 50. The method according to claim 49, wherein the first film of step (ii) is first annealed in the presence of the inert gas at a temperature of from 500 to 550°C.
- 25 51. The method according to claim 49, wherein the first film is first annealed in the presence of the inert gas for a period of from 10 to 60 minutes.
- 30 52. The method according to claim 48, wherein the first film of step (ii) is subsequently annealed in the presence of a source of VI_A₁ for at least 30 minutes.
53. The method according to claim 52, wherein the first film of step (ii) is annealed in the presence of a source of VI_A₁ at a temperature of 500°C.

54. The method according to either one of claims 44 and 46, wherein IB is Cu, IIIA₁ is In, IIIA₂ is Ga, VIA₁ is Se.

55. The method according to claim 54, wherein the quaternary alloy has a formula (II)



56. The method according to claim 54, wherein a source of Se is a gaseous mixture of H₂Se and at least one inert gas.

57. The method according to claim 56, wherein the molar concentration of Se relative to the at least one inert gas is 0.12%.

58. The method according to claim 44 which is for producing a group IB-III A-VIA quaternary alloy semiconductor film, and wherein:

- step (i) comprises providing a metal film comprising a mixture of Cu, In and Ga in elemental or alloy form;
- step (ii) comprises heat treating the metal film in the presence of a gaseous mixture of H₂Se and at least one inert gas, wherein the molar concentration of Se relative to the at least one inert gas is from 0.05 to 0.3%, at a temperature of 400°C, for a period of between 30 to 60 minutes, so as to form a mixture of binary alloys in the form of CuSe, InSe, Ga₂Se₃ and a ternary alloy in the form of a CuInSe₂ alloy.

- subjecting the first film of step (ii) to the following consecutive steps:
 - 5 o a first heat treatment step comprising heat treating the first film of step (ii) to a reaction temperature from 500°C to 550°C in 15 to 30 minutes;
 - 10 o a second heat treatment step comprising first annealing the first film of step (ii) in Ar(g) at a reaction temperature from 500°C to 550°C for at least 15 minutes; and then secondly annealing the first film of step (ii) in the presence of a gaseous mixture of H₂Se and Ar(g), wherein the molar concentration of Se relative to Ar is 0.12% so as to form a quaternary alloy having the general formula (II).
59. The method according to claim 1, which is for producing a group IB-IIIA-VIA quaternary alloy semiconductor film, and wherein:
- 20 - step (i) comprises providing a metal film including a mixture of at least one group IB element and a group IIIA element;
 - 25 - step (ii) comprises heat treating the metal film of step (i) in the presence of a source of VIA₁ under conditions to form a first film comprising a mixture of binary alloys selected from the group consisting of a group IB-VIA₁ alloy, a group IIIA-VIA₁, and a ternary alloy being a group IB-IIIA-VIA₁ alloy; and
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- step (iv) comprises heat treating the first film of step (ii) in the presence of a source of VIA_2 so as to form a group IB-IIIA- VIA_1 - VIA_2 quaternary alloy semiconductor film.

5 60. The method according to claim 59, wherein step (iv) comprises a first heat treatment step wherein the first film of step (ii) is heated and then subsequently a second heat treatment step wherein the first film of step (ii) is annealed so as to form a group IB-IIIA- VIA_1 - VIA_2 quaternary alloy.

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61. The method according to claim 60, wherein the first heat treatment step of step (iv) comprises heating the first film of step (ii) to a reaction temperature from 100 to 600°C.

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62. The method according to claim 60, wherein the second heat treatment step of step (iv) comprises annealing the first film of step (ii) in the presence of a source of VIA_2 .

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63. The method according to claim 62, wherein the first film of step (ii) is annealed in the presence of the source of VIA_2 at a temperature from 100 to 600°C.

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64. The method according to claim 63, wherein the first film of step (ii) is annealed in the presence of the source of VIA_2 at a temperature from 500 to 550°C.

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65. The method according to claim 64, wherein the first film of step (ii) is annealed in the presence of a source of VIA_2 at a temperature of 500°C.

66. The method according to claim 62, wherein the first film of step (ii) is annealed in the presence of a source of VIA_2 for at least 30 minutes.

67. The method according to either one of claims 59 and 60, wherein IB is Cu, the group IIIA element is In, VIA₁ is Se, VIA₂ is S.

5 68. The method according to claim 67, wherein the quaternary alloy has a formula (III);



10 69. The method according to claim 67, wherein a source of S is a gaseous mixture of H₂S and at least one inert gas.

70. The method according to claim 69, wherein the molar concentration of S relative to the at least one inert gas is
15 0.35 molar percent.

71. The method according to claim 59 which is for producing a group IB-IIIA-VIA quaternary alloy semiconductor film, and wherein:
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- step (i) comprises providing a metal film comprising a mixture of Cu and In in elemental or alloy form;
- step (ii) comprises heat treating the metal film in the presence of a gaseous mixture of H₂Se and at least one inert gas, wherein the molar concentration of Se relative to the at least one inert gas is from 0.05 to 0.3% for a period of between 30 to 60 minutes, so as to form a mixture of binary alloys in the form of CuSe and InSe and
25 a ternary alloy, namely CuInSe₂; and
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- step (iv) comprises subjecting the first film of step (ii) to the following consecutive steps:

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- o a first heat treatment step comprising heat treating the first film of step (ii) to a reaction temperature from 500°C to 550°C in 15 to 30 minutes;

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- o a second heat treatment step comprising annealing the first film of step (ii) in the presence of a gaseous mixture of H₂S and Ar(g), at a temperature of from 500°C to 550°C, wherein the molar concentration of S relative to Ar is 0.35% so as to form a quaternary alloy having the general formula (III).